

**NASA TECHNICAL NOTE**



**NASA TN D-3502**

*C. 1*

LOAN COPY: RETURN  
AFWL (WLIL-2)  
KIRTLAND AFB, N M



**NASA TN D-3502**

# **SHOCK-TUBE INVESTIGATION OF BROMINE DISSOCIATION RATES IN PRESENCE OF ARGON, NEON, AND KRYPTON**

*by Marvin Warshay*  
*Lewis Research Center*  
*Cleveland, Ohio*





SHOCK-TUBE INVESTIGATION OF BROMINE DISSOCIATION RATES  
IN PRESENCE OF ARGON, NEON, AND KRYPTON

By Marvin Warshay

Lewis Research Center  
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

---

For sale by the Clearinghouse for Federal Scientific and Technical Information  
Springfield, Virginia 22151 - Price \$1.00

# SHOCK-TUBE INVESTIGATION OF BROMINE DISSOCIATION RATES

## IN PRESENCE OF ARGON, NEON, AND KRYPTON

by Marvin Warshay

Lewis Research Center

### SUMMARY

A shock tube with an all-glass driven section was employed to obtain dissociation rates of bromine in dilute mixtures (1 percent) with three noble gases (argon, neon, and krypton). All rate measurements were made behind incident shocks. The temperature range was  $1200^{\circ}$  to  $1900^{\circ}$  K. Extensive theoretical treatments have recently been applied to dissociation and recombination of gases; however, evaluation of these theories and continued progress have been hampered both by the lack of data and by the poor quality of data obtained in shock tubes.

For bromine, poor quality shock-tube data had resulted from difficulties involving three critical areas: materials of construction, light absorption measurements, and temperature drop during dissociation. In this investigation the experimental difficulties were overcome by using a carefully designed apparatus and procedure.

This investigation provided entirely new data, the rates of dissociation of bromine in the presence of neon and of krypton, as well as more reliable dissociation rates of bromine in argon. These data helped in the evaluation of the abilities of theoretical models to predict halogen dissociation-recombination rates in the presence of noble gases. The five models evaluated were by Bunker and Davidson; Light; Nielsen and Bak; Benson, Fueno, and Berend; and Keck and Carrier. For the recombination portion of the evaluation, published data were used. The model which best predicts the collision partner effects is by Benson, Fueno, and Berend. However, one apparent defect that all models have is the inability to predict the bromine experimental activation energy  $E_a$ , which for the simple collisional kinetic form of the dissociation-rate constant is less than the dissociation energy  $D_0$ . This situation exists because, in all but the Bunker-Davidson model,  $E_a$  is assumed to equal  $D_0$ .

## INTRODUCTION

In the past decade the shock-wave method has been used extensively in the field of chemical kinetics; it has been of particular value in the measurement of the rates of dissociation of diatomic molecules. These experimental results have heightened interest in the theory of dissociation and recombination. A great number of theoretical models have been proposed in recent years which attempt to treat various aspects of the mechanisms of dissociation and recombination, and in some cases, to predict the rates of dissociation and recombination of simple species (refs. 1 to 8). Proper evaluation of these theories and continued progress in these areas have been hampered by two problems. First, many experimental data are still lacking. Second, as Palmer succinctly expressed it (ref. 9), ". . . shock tube measurements of rate constants have been notoriously imprecise."

The results of past investigations of dissociation of bromine in the presence of argon clearly fit Palmer's description. Figure 1 shows that the agreement among the four dif-

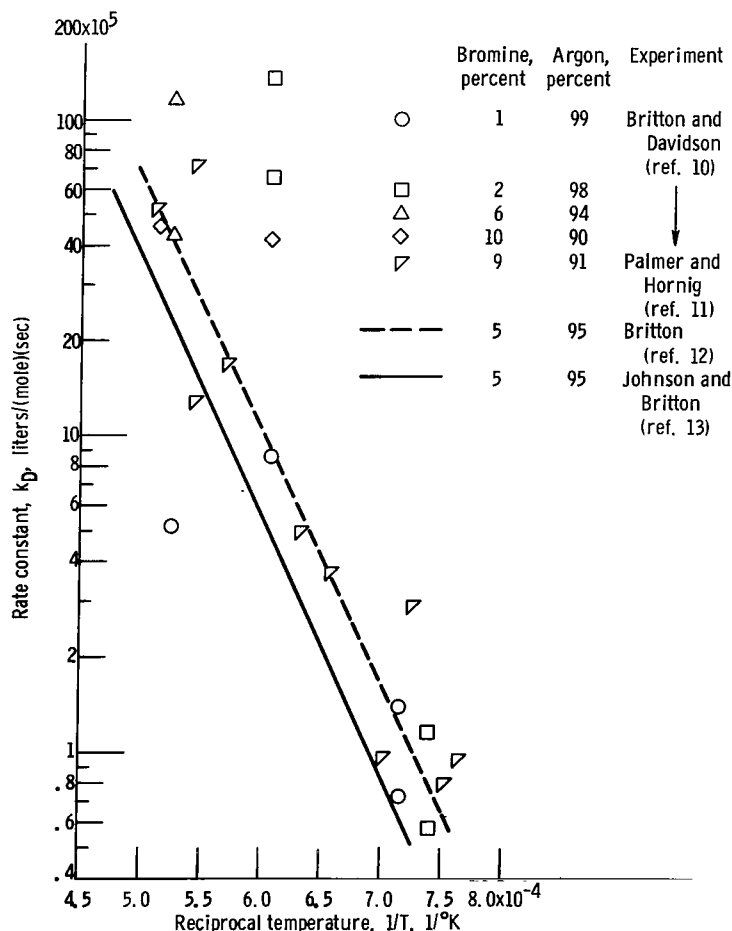


Figure 1. - Rate constants for dissociation of bromine in bromine-argon mixtures. (Not all experimental data included for refs. 10 and 11.)

ferent investigations (refs. 10 to 13) is not good and the scatter of the data of several of the investigations is pronounced. For example, although the fourth investigation (ref. 13) is a repeat of the third investigation (ref. 12), with the same equipment, there is approximately a 50-percent discrepancy between the dissociation-rate constants at the same temperature.

Despite the previous inadequacies, the outlook for making reliable measurements of bromine dissociation rates is not bleak. Bromine, in several respects, is a convenient substance with which to work. It dissociates at relatively low temperatures. It absorbs light strongly in the visible region and provides a good means of following the course of a reaction. In addition, from careful analysis of past bromine shock-tube experiments, major trouble areas were uncovered. These critical areas are associated with bromine-metal contact, light-absorption measurements, and cooling of the gas as dissociation proceeds.

In the present study of bromine dissociation, the problems that had plagued past investigations were largely overcome. An apparatus and a procedure were carefully designed to obtain reliable bromine dissociation-rate data. These new rate data, which include three different noble-gas collision partners (argon, neon, and krypton), helped to make possible meaningful comparisons of five theoretical models. For completeness, a comparison was also made with recombination data from the literature.

The dissociation and recombination of halogens in the presence of noble gases are among the simpler dissociation and recombination processes. Establishing whether or not a model successfully predicts the rates in the elementary case aids the development of a theoretical model which will be able to make accurate predictions in the complex case.

## SYMBOLS

A	preexponential constant in dissociation-rate constant equation
$C_p$	mean heat capacity of gas at constant pressure
$C_v$	mean heat capacity of gas at constant volume
$D_0$	dissociation energy at 0° K
$E_a$	activation energy in dissociation-rate constant equation
F	Palmer-Hornig enthalpy correction coefficient
$\dot{f}$	time derivative of fraction of dissociation
H	defined by equation (6)

$I$	transmitted light intensity
$I_0$	incident light intensity
$I_1$	transmitted light intensity prior to passage of shock front
$I_2$	transmitted light intensity following passage of shock front
$K$	equilibrium constant
$k_{\text{cal}}$	calculated dissociation-rate constant
$k_D$	dissociation-rate constant
$k_{\text{obs}}$	observed dissociation-rate constant
$k_R$	recombination-rate constant
$\ell$	optical path length
$M$	collision partner
$N$	total excited vibrational state of $X_2$
$n$	vibrational state of $X_2$
$P_1$	initial pressure of mixture in driven section
$R$	gas constant
$T$	absolute temperature
$T_1$	absolute gas temperature prior to passage of shock front
$T_2$	absolute gas temperature following passage of shock front
$\dot{T}_2$	time derivative of absolute temperature following passage of shock front
$V_1$	velocity of unshocked gas relative to shock front
$V_2$	velocity of shocked gas relative to shock front
$W$	mean molecular weight
$X$	atom
$X_0$	mole fraction of bromine in shocked gas
$X_2$	diatomic species
$X_2^*$	internally (vibrationally and rotationally) excited species in unbound state
$X_2^{(n)}$	intermediate species in $n^{\text{th}}$ vibrational state
$\epsilon$	extinction coefficient of bromine
$\epsilon_2$	extinction coefficient of bromine in shocked gas

$\rho_2$	density of shocked gas
$\dot{\rho}_2$	time derivative of density of shocked gas
$\tau$	laboratory time
$[ ]$	concentration
$\{ \dot{\cdot} \}$	time rate of change in concentration due solely to chemical reaction

## EXPERIMENTAL CONSIDERATIONS

In the following discussion of experimental apparatus and procedures many points are treated only briefly because they are well understood and have been discussed at length in other papers (refs. 11, 14, and 15). However, at the beginning of each subsection an effort is made to stress the pertinent aspects of the design and/or procedure.

### Shock Tube

The significant feature of the shock-tube design was the avoidance of all contact of bromine with metal surfaces. Palmer and Hornig (ref. 11) were able to detect their pure bromine test gas reacting with aluminum diaphragms. In the present study, preliminary experiments indicated that bromine has a strong affinity for both copper and stainless steel. After a 1-percent-bromine - 99-percent-argon mixture was injected into one end of the 12-foot (3.66-m) stainless-steel section, the bromine concentration of the mixture at the opposite end required approximately 20 minutes to rise to its ultimate value (fig. 2).

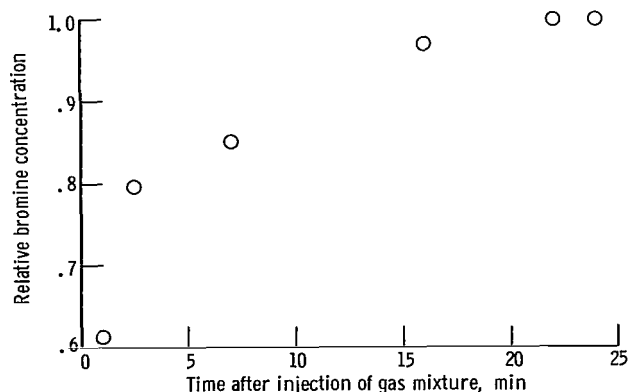


Figure 2. - Measured bromine concentrations of 1-percent-bromine - 99-percent-argon mixtures in stainless-steel shock-tube driven section.

Therefore, with common metals completely ruled out and with tetrafluoroethylene polymer (TFE) commercially unavailable in the size needed, the logical choice for the driven section was glass. With glass, unlike metal, there was no detected delay period for a bromine mixture to equilibrate.

The main components of the shock tube used in this investigation were a 6-foot (1.83-m) driven section made of stainless steel and a 9-foot (2.74-m) driven section made of borosilicate glass

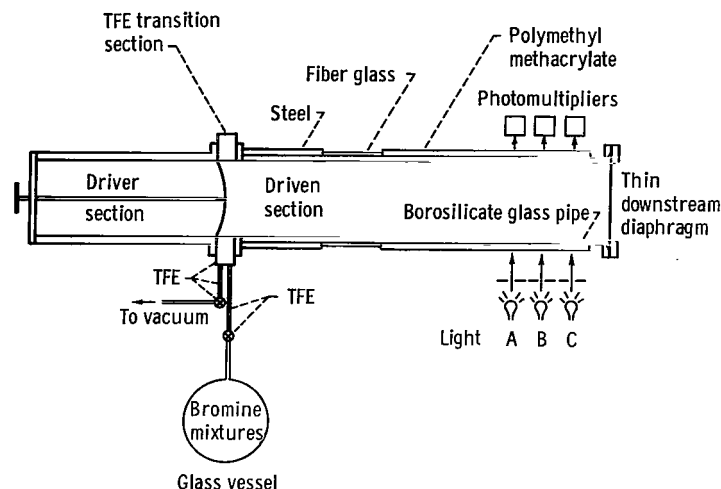


Figure 3. - Schematic diagram of shock tube.

pipe (fig. 3). Both sections had an inner diameter of 4 inches (10.16 cm). Placed between the two sections, on the low-pressure side of the diaphragm, was a 1-inch-long (2.54-cm) transition section made of TFE. The vacuum and gas sample lines were connected to this section rather than directly to the glass driven section.

The entire gas mixture line and the initial portions of the vacuum lines leading from the shock tube consisted of TFE tubing, fittings, and valves. These TFE valves were used to prevent the bromine gas samples from coming into contact with the metal portion of the vacuum lines.

The glass wall of the driven section was strengthened in order to increase the pressure range over which the tube could be used. Strengthening was accomplished by joining materials to the outside of the glass; this added tensile strength to the glass walls. Three materials were joined to the outside of the glass at different locations along the pipe. The first 18 inches (45.72 cm) of driven section were covered by a steel tube which was bonded to the glass with epoxy cement. The next 12 inches (30.48 cm) of glass were wound with adhesive-backed fiber-glass tape. The remaining length of driven section was strengthened by a 1/2-inch-thick (1.27-cm) polymethylmethacrylate tube that had been split lengthwise to allow it to fit over the end of the glass pipe and was kept tightly pressed against the glass by means of several clamps. Polymethylmethacrylate is convenient because it is transparent. Of the three methods, the fiber-glass method is considered to impart the greatest strength to the glass because of the intimate contact between the two substances.

A stainless-steel flange was located between the borosilicate glass pipe and the TFE transition section. This flange was installed as a substitute for the end of the glass pipe which broke off during preliminary experiments at a driver pressure of 140 pounds per square inch gage ( $9.84 \text{ kg/cm}^2$ ). The very small area of metal flange that was exposed to



the gas mixture was covered with a type of monochlorotrifluoroethylene polymer grease which was experimentally determined to be inert to bromine.

A thin inert polyethylene terephthalate sheet was used as a closure. Beyond this was a pipe which led to the exhaust stack. By breaking through this sheet the shock itself provided the means of disposing of the shock-tube contents.

The driver section was fitted with a solenoid-operated piercing mechanism which was used to pierce the polyethylene terephthalate diaphragms. Multiple diaphragms were used to obtain the desired rupture strengths. The pressure of the helium driver gas was raised to within 3 pounds per square inch gage ( $0.21 \text{ kg/cm}^2$ ), or less, of the diaphragm bursting pressure, which was 80 pounds per square inch gage ( $5.62 \text{ kg/cm}^2$ ) in most experiments. In practically all cases, Mach number and temperature variations were produced by varying the initial driven gas pressures.

## Gas Mixtures

In the preparation of the mixtures of bromine and noble gas in the gas-handling apparatus, bromine came into contact only with glass and TFE surfaces. The valves, fittings, and tubing were TFE.

Calibrated Bourdon tube gages were used to prepare the 1-percent-bromine mixtures by the partial-pressure method. A buffer of the appropriate noble gas was used to keep bromine out of the gage and metal line.

The gas mixture bottles were large borosilicate glass boiling flasks whose walls were strengthened by bonding fiber-glass gauze to them with epoxy cement. From the measured tensile strength of a test specimen of the glass-epoxy bond, it was calculated approximately that the strengthened walls of the glass bottle would withstand pressures up to 800 pounds per square inch ( $56.24 \text{ kg/cm}^2$ ). Allowable gas bottle pressure was then limited by the TFE valve connected to the bottle; this valve was capable of withstanding a pressure of 150 pounds per square inch gage ( $10.55 \text{ kg/cm}^2$ ). If properly applied to the glass portion of the shock tube, this method of glass strengthening might allow the shock tube to be used at far greater pressures than are presently being considered.

Reagent grade bromine (99.5-percent minimum purity) was further purified by distillation before it was used. The argon, neon, and krypton purities were 99.998, 99.96, and 99.994 percent, respectively. Each mixture was prepared 1 week before use to allow time for thorough mixing.

## Instrumentation

Keeping the incident light intensity  $I_0$  within narrow bounds was a very important

part of the measurements of the bromine concentration by the light-absorption technique. Wray (ref. 16) has pointed out that the largest source of error in the use of absorption spectrometry for the present type of application is the measurement of  $I_0$ . Jacobs and Giedt (ref. 17), who used an expression for calculating the dissociation rate of chlorine involving the term  $\log \log (I_0/I)$ , estimated that a maximum error of 30 to 40 percent in  $k_D$  could result from an error of only 2 percent in  $I_0$ . The magnitude of the error in  $k_D$  that results from an error in  $I_0$  depends on the particular expression used to calculate this rate constant as well as on the conditions, principally the concentration. For the type of expression used for calculating  $k_D$  in both the present bromine investigation and in references 10 to 14, the error is smaller for lower bromine concentrations.

The determination of  $I_0$  hinges on both the apparatus and the procedures used. The critical features of apparatus are stable power supplies and light sources, a photomultiplier system that produces stable signals with high signal-to-noise ratios, and a good device to measure the  $I_0$  signal.

The incandescent light source (6.5-V, 2.75-A light B, fig. 3) powered by a highly regulated power supply gave extremely good stability, with less than 0.05 percent change per hour for either the power-supply voltage or the bulb current. The light beam was collimated by placing the bulb at the focal point of a double-convex lens. This lens was mounted in a camera shutter which served to regulate the exposure of the shock tube and the detection system to the light beam. A fixed 0.635-millimeter slit was used where the beam entered the shock tube. The light emerging from the shock tube passed through an interference filter that fed monochromatic light into the 931A photomultiplier. The measured peak and band width at the filter half-peak were 4400 Å and 80 Å, respectively. The high voltage required to operate the photomultiplier was produced by a very stable power supply (<0.01 percent change/hr). The photomultiplier output was recorded by the lower beam of a dual-beam oscilloscope. An oscilloscope camera was used to photograph the oscilloscope traces.

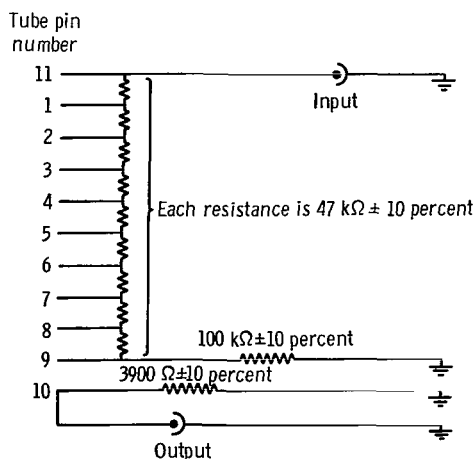


Figure 4. - 931A photomultiplier circuit diagram.

The ideal photomultiplier system would respond instantaneously to an input signal and would produce a stable signal with no noise. Unfortunately, time response, minimization of phototube fatigue, and high signal-to-noise ratios are goals which often require opposing actions. For example, to minimize fatigue and still maintain a high output would require a high output impedance in the circuit; however, good time response requires a low output impedance. The photomultiplier system developed for this work produced low fatigue rates (0.01-percent signal change/msec), good rate response (0.7 μsec), and good signal-to-

noise ratios (up to 100). The photomultiplier circuit diagram is shown in figure 4.

It was also important not to expose the photomultiplier indiscriminately to the light. The shutter which was blocking light from the phototube was controlled by a solenoid connected to a timing mechanism. (This timing mechanism also controlled the solenoid that operated the piercing mechanism.) Keeping the duration of each light exposure as low as possible was not the only thing that was necessary to minimize fatigue. Intervals between exposures that were too short resulted in erratic rates of decay of  $I_0$ . Therefore, the exposure duration was less than 0.1 second and the interval between exposures was of the order of 15 minutes. (The higher the anode current, the greater the required interval between exposures.) Measurements of  $I_0$  were made both before and after each shock; the  $I_0$  at the time of the shock was calculated by interpolation. In most cases the deviation in  $I_0$  was within  $\pm 0.5$  percent. The traces were measured on a time-motion analyzer.

Two additional light beams (A and C, fig. 3) together with associated optical equipment, like that just described, were located 6 inches (15.24 cm) on either side of the light (B) that was used to measure bromine concentration. The signal from light A, which was 24 inches (60.96 cm) from the end of the shock tube, was used to trigger the oscilloscope. Photomultiplier signals from lights A and C were used to measure the shock velocity. With the aid of a cathetometer, all three beams were carefully aligned perpendicular to the shock-tube axis.

## RESULTS

### Extinction Coefficients of Bromine

The static measurement of the room-temperature extinction coefficient  $\epsilon$  served to test the efficacy of the optical and electronic equipment that was to be used later in the shock-wave measurements. The value of  $\epsilon$  found for the  $\log_{10}$  form of the Beer-Lambert law was  $144.5 \pm 1.6$  liters per centimeter-mole.

The measurements of  $\epsilon$  were considerably less scattered than those made by other investigators (refs. 10 to 12), who reported uncertainties as high as  $\pm 15$  percent. Part of the reason for their poorer precision lies in the fact that these measurements were made directly in the shock tube, in some cases prior to the shocks, while those of the present investigation were carried out in a precision absorption cell connected to the gas handling apparatus. In the latter case, better control is achieved over  $I/I_0$  and the bromine partial pressure, two of the principal parameters that determine  $\epsilon$ .

The experimental determination of  $\epsilon$  at elevated temperatures was conducted from

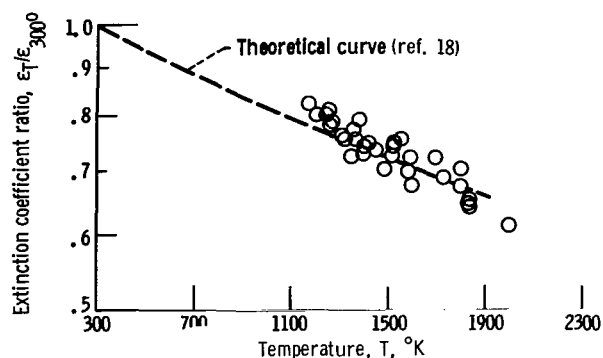


Figure 5. - Temperature dependence of bromine extinction coefficient at 4400 Å.

shock-tube experiments in the conventional manner, that is, from the initial absorption of light caused by the shock wave. These data are shown in figure 5. The dashed line was calculated from the theoretical expression of Sulzer and Wieland (ref. 18); the agreement is good. Furthermore, the scatter of the data is lower than that of most other investigations of this kind.

## Calculations

The rate constant for the dissociation of bromine



is defined by

$$-\left\{\dot{\text{Br}}_2\right\} = k_D [\text{Br}_2][\text{M}] \quad (2)$$

No contribution from the reverse reaction appears in equation (2) since only initial rates were measured in this experiment. Also, because of the small concentration of bromine used, its contribution as a collision partner is ignored. Equation (3) expresses  $k_D$  in terms of quantities which are either calculable or measurable:

$$k_D = \frac{\left(\frac{dI_2}{d\tau}\right) \left(\frac{V_2}{V_1}\right) F}{I_0 \frac{I_2}{I_0} \epsilon_2 \ell [\text{Br}_2][\text{M}]} \quad (3)$$

This equation is very similar to the expressions used by other investigators (refs. 11 and 19).

## Temperature Drop During Dissociation

The dissociation of bromine is an endothermic reaction; consequently, the gas mixture cools as dissociation proceeds. This cooling leads to a change in all the parameters characterizing the gas in the reaction zone and must be taken into account to evaluate the rate constants properly. Palmer and Hornig (ref. 11) derived a factor, which they called  $F$ , to make this enthalpy correction. However, for their 1-to-10 bromine-argon mixture, their corrections varied nonlinearly with temperature between the extremes 50 and 690 percent ( $1.50 \leq F \leq 7.90$ ). Though theoretically correct, the determination of  $F$  involves uncertainties that are a reflection of the uncertainties associated with the components that make up  $F$ , such as temperature and extinction coefficients. Therefore, the most satisfactory solution is to minimize temperature drop, and thereby make its influence minor. At the 1-percent-bromine concentrations used in the present investigations the enthalpy corrections were small and varied little with temperature ( $1.07 < F < 1.13$ ).

Hiraoka and Hardwick (ref. 19) have written a convenient expression for the  $F$  correction factor:

$$F = \frac{1}{1 - \frac{\dot{\rho}_2}{\rho_2} \frac{1}{\dot{f}} - \frac{d \ln(\epsilon_2 \ell)}{dT_2} \frac{\dot{T}_2}{\dot{f}}} \quad (4)$$

For a very small fraction of bromine dissociated, they derived equations for the changes in density and temperature as the dissociation progresses; the ideal gas law was assumed and the conservation laws for mass, momentum, and energy were used:

$$\frac{\dot{\rho}_2}{\rho_2} \frac{1}{\dot{f}} = \frac{X_0(\Delta H - C_v T_2)}{C_p T_2 - \left(\frac{W}{R}\right) V_2^2 C_v} \quad (5)$$

where

$$\Delta H = D_0 - \frac{RT_2}{2} \quad (6)$$

$$\frac{\dot{T}_2}{\dot{f}} = \frac{\dot{\rho}_2}{\rho_2} \frac{1}{\dot{f}} \left( \frac{W}{R} V_2^2 - T_2 \right) - X_0 T_2 \quad (7)$$

In these calculations the shock-wave parameters were calculated with the standard one-dimensional relations (ref. 15). Table I contains calculated and measured quantities used in a representative calculation of  $k_D$ .

## Measured Rate Constants

With the aid of equations (3) to (7), bromine dissociation-rate constants were calculated for each of the three systems, bromine-argon ( $\text{Br}_2\text{-Ar}$ ), bromine-neon ( $\text{Br}_2\text{-Ne}$ ), and bromine-krypton ( $\text{Br}_2\text{-Kr}$ ). These data are presented in figure 6, in the traditional manner of  $\log k_D$  against  $1/T$ . The least-squares lines representing the data were calculated by assuming the simple collisional form for  $k_D$ , that is,  $AT^{1/2} \exp(-E_a/RT)$ . The equations for the three systems are as follows:

$\text{Br}_2\text{-Ar}$

$$k_D = 2.18 \times 10^8 T^{1/2} \exp[(-31.5 \text{ kcal/mole})/RT] \quad \text{liters}/(\text{mole})(\text{sec}) \quad (8)$$

$\text{Br}_2\text{-Ne}$

$$k_D = 1.82 \times 10^8 T^{1/2} \exp[(-31.3 \text{ kcal/mole})/RT] \quad \text{liters}/(\text{mole})(\text{sec}) \quad (9)$$

$\text{Br}_2\text{-Kr}$

$$k_D = 4.32 \times 10^8 T^{1/2} \exp[(-33.6 \text{ kcal/mole})/RT] \quad \text{liters}/(\text{mole})(\text{sec}) \quad (10)$$

The data for each of the three systems exhibit definite linear trends over wide temperature ranges. Furthermore, the precision of the data is significantly higher than that of most published data for bromine dissociation rates in the presence of argon. (Compare figs. 1 and 6.) In figure 6, the mean  $|k_{\text{obs}} - k_{\text{cal}}|/k_{\text{obs}}$  values for the  $\text{Br}_2\text{-Ar}$ ,  $\text{Br}_2\text{-Ne}$ , and  $\text{Br}_2\text{-Kr}$  systems are 13, 11, and 9 percent, respectively.

Separate experiments conducted with the light source turned off showed that emission from the shock heated gas could be ignored in the absorption experiments. Also, Britton (ref. 12) reported that below  $1900^\circ \text{K}$  bromine emission is negligible.

## THEORETICAL MODELS

Only those models which can be used for the calculations for the specific halogen reactions investigated in this study were considered. Therefore, Keck's model (ref. 8)

TABLE I. - CALCULATED AND MEASURED  
QUANTITIES USED IN REPRESENTATIVE  
CALCULATION OF BROMINE DISSOCI-  
ATION RATE CONSTANT

$T_1$ , °K	300.4
$P_1$ , mm Hg	26.1
$dI_2/d\tau$ , arbitrary units/sec	$55.4 \times 10^5$
$V_1$ , m/sec	1301.2
$V_2$ , m/sec	380.4
$I_0$ , arbitrary units	2701
$I_1/I_0$	0.954
$I_2/I_0$	0.902
$\epsilon_{2^\ell}$ , liters/mole	2161
$[Br_2]$ , moles/liter	$4.770 \times 10^{-5}$
$[Ar]$ , moles/liter	$4.727 \times 10^{-3}$
$\dot{\rho}_2/\rho_2 \dot{i}$	0.0547
$\frac{\dot{T}_2}{\dot{i}} \frac{d \ln(\epsilon_{2^\ell})}{dT_2}$	0.0179
F	1.078
$k_D$ , liters/(mole)(sec)	$1.48 \times 10^6$
$T_2$ , °K	1825

was not included because it only predicts upper bounds to the rates. In addition, it was necessary to be able to extract from each model absolute rate constants rather than merely an expression for the rate constant in terms of unknown parameters. In some cases these calculations were facilitated by calculations of some of the parameters by the authors themselves. A review of recent literature indicated that five models should be considered in this work. These are the models of Bunker and Davidson; Light; Nielsen and Bak; Benson, Fueno, and Berend; and Keck and Carrier (refs. 1 to 6). The Benson-Fueno-Berend model was originated by Benson and Fueno (ref. 4); later, however, Berend joined Benson and participated in the subsequent work on the model (ref. 5). This group of five models includes some which were derived specifically for recombination or for dissociation or, in one case, for both. However, at any particular temperature, microscopic reversibility, that is,  $K = k_D/k_R$ , permits comparisons among the models on the basis of either recombination or dissociation rates. At room temperature the calculated theoretical values will be compared with published experimental re-

combination rates for halogens in the presence of noble gases. In the temperature range where dissociation is significant the comparison will be made by using the dissociation rates measured in the present investigation.

The models of Bunker and Davidson and of Benson, Fueno, and Berend are recombination models. Bunker and Davidson's theory is for the rate of recombination of halogen atoms  $X$  in the presence of various third bodies  $M$ . The theory assumes the formation of an equilibrium concentration of  $MX$  species. On the other hand, the recombination model of Benson, Fueno, and Berend does not involve complexes with the atoms. Their mechanism involves a cascade model in which deactivation occurs by small amounts, essentially one vibrational quantum, at a time. A fundamental difference between these two chemical mechanisms can be illustrated by equations expressing their initial basic assumptions:

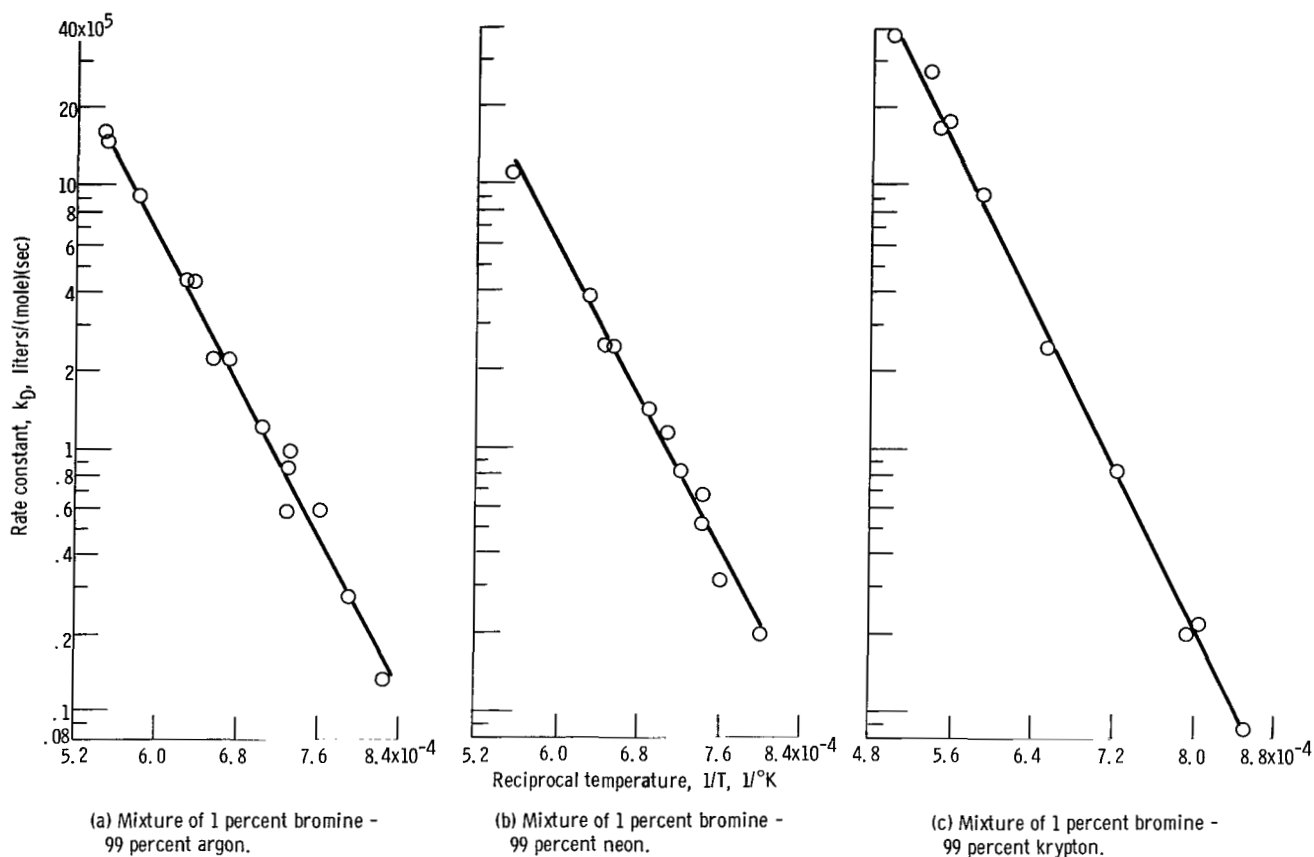
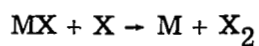
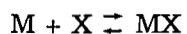
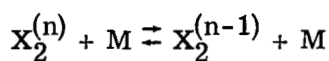
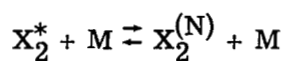
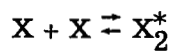


Figure 6. - Rate constants for dissociation of bromine.

### Bunker-Davidson



### Benson-Fueno-Berend



$$n = 1, 2, 3, \dots, N$$

Light and Nielsen and Bak used classical scattering approaches in their models for



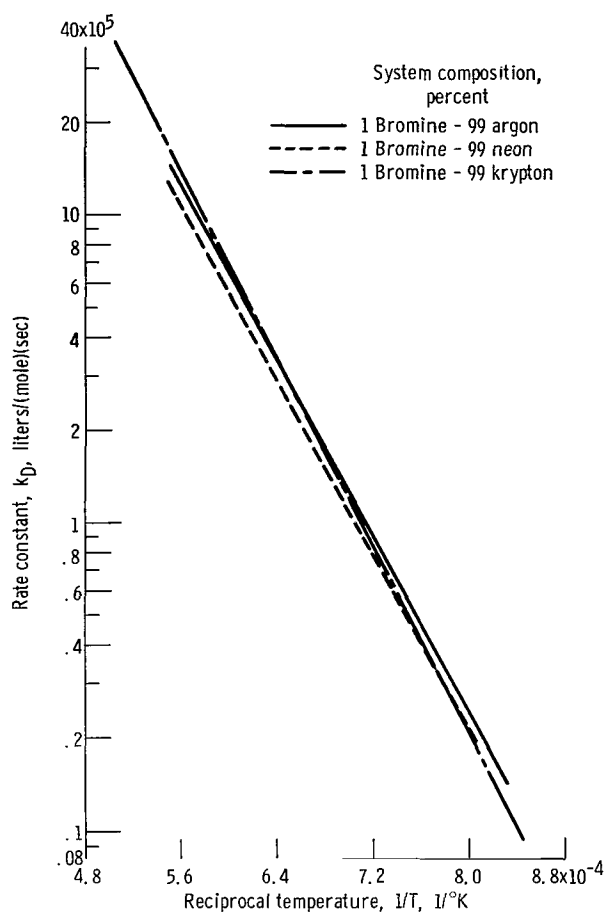


Figure 7. - Least-squares lines for bromine dissociation rate constant data for argon, neon, and krypton systems.

dissociation of gaseous diatomic molecules. In the former case the collisions were assumed to be adiabatic, while in the latter case they were assumed to be strongly nonadiabatic. In addition, the model of Nielsen and Bak involves only monatomic third bodies.

The mechanism of Keck and Carrier is the most general; it is based on a theory of nonequilibrium dissociation and recombination. They set up a master equation to investigate the coupled vibration, dissociation, and recombination of a dilute mixture of diatoms in a medium of inert gas atoms. Examination of classical and quantum models showed that a classical model is a better approximation to the physicochemical phenomena. In their theory, Keck and Carrier did not take into account the Van der Waals forces, which are important at low temperatures. For this reason their theory will be left out of any comparisons involving low-temperature rate data.

These theoretical models have some characteristics in common. Regarding

temperature dependency, the relations developed by the three dissociation models are basically of the simple collision form. In addition, the dissociation models, along with the Benson-Fueno-Berend model, assume that  $E_a = D_0$ .

## DISCUSSION

The least-squares lines representing the bromine experimental data for the three systems investigated are plotted in figure 7. These lines indicate that bromine dissociation is approximately 13 percent slower in neon than in argon. The krypton system results were rather unexpected; they indicated that at high temperatures bromine dissociated at higher rates in the presence of krypton than in the presence of argon, while the reverse was true at low temperatures.

Before these results are used in the evaluation of the theoretical models, they should

be considered in relation to the problem concerning the scarcity of reliable rate data. For instance, there are no published experimental data which could have been used to predict successfully these collision partner effects. An investigation (ref. 20) of the dissociation of fluorine was conducted in the presence of argon, neon, and krypton; the neon data were completely reported, but for the argon and krypton systems, only general trends were mentioned in the discussion. Halogen dissociation experiments (refs. 12 and 14) containing results which could be used for satisfactory comparison of noble gas effects on dissociation rates have been carried out only with argon and helium systems. As for halogen recombination, only iodine recombination experiments have been conducted in the presence of several noble gases. Even if the third-body efficiencies were assumed to be the same for all halogens, it would be wrong simply to equate the efficiencies obtained for recombination at low temperatures with those obtained for dissociation at high temperatures. The values vary with temperature and, at present, in an unpredictable manner.

For example, for recombination of iodine at room temperature, the relative efficiency of helium compared with that of argon has been reported to be 36 percent (ref. 21) and 48 percent (ref. 22). On the other hand, at the higher temperatures where dissociation is important, Britton, Davidson, Gehman, and Schott (ref. 14) reported a widely varying relative efficiency between helium and argon; it was 74 percent at  $1000^{\circ}\text{K}$  and only 32 percent at  $2000^{\circ}\text{K}$ .

Finally, to generalize from the collision partner efficiencies of neon and krypton in the dissociation of nonhalogen diatomic gases is also unwise, for two reasons. First, the dissociation results for hydrogen, deuterium, nitrogen, and oxygen disclose no apparent pattern. For example, with respect to oxygen dissociation, Rink (refs. 23 and 24) found krypton to be twice as efficient as argon; however, for hydrogen dissociation, he could detect no difference in the efficiencies of krypton and argon (ref. 25). Second, the poor precision of much of the diatomic dissociation data ( $\pm 30$  to  $\pm 50$  percent) would make the rate data rather unreliable.

## Absolute Dissociation Rate Constants

The predictions of the dissociation rates of bromine in the presence of argon for all five models, as well as the line representing the experimental data of this investigation, are plotted in figure 8. (Benson and Fueno calculate four different cases; graphed in figure 8 is case IB which uses a Morse function and is the one whose prediction comes closest to the experimental data.) At the same temperatures, four of the five theoretical predictions are within an order of magnitude of the experimental values. The Keck-

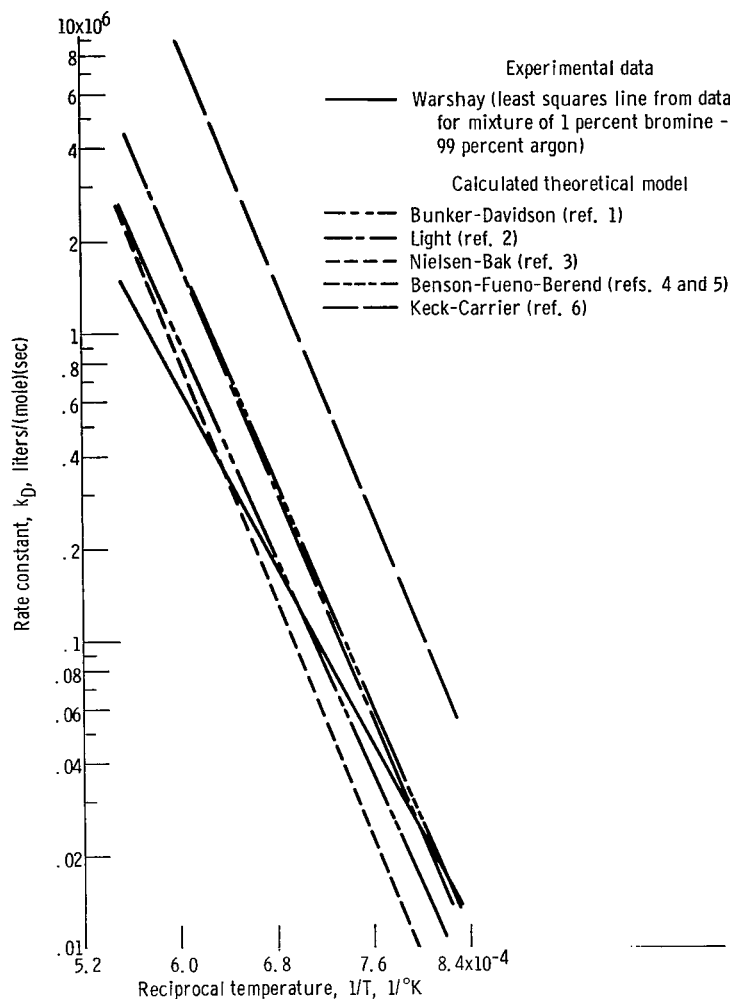


Figure 8. - Rate constants for dissociation of bromine in bromine-argon mixture.

Carrier model predicts much higher rates than those predicted by the other four models or those which had been measured.

However, it is equally important to point out the discrepancies between the predicted and the experimental rates. For instance, the slopes of all five predicted lines are steeper than the experimental line; this difference in slopes indicates that, from the standpoint of a simple kinetic collision model, the activation energies in the five models are higher than that observed. These differences between the measured and predicted slopes are more evident when the rate constants are converted to recombination constants. Figure 9 shows that the typical inverse temperature dependence of the experimental rate constants is much more pronounced than is predicted by any of the models. This discrepancy is due to the assumption, which is made in all but the Bunker-Davidson model, that  $E_a = D_0$ . As has been mentioned previously, the measured activation energy for

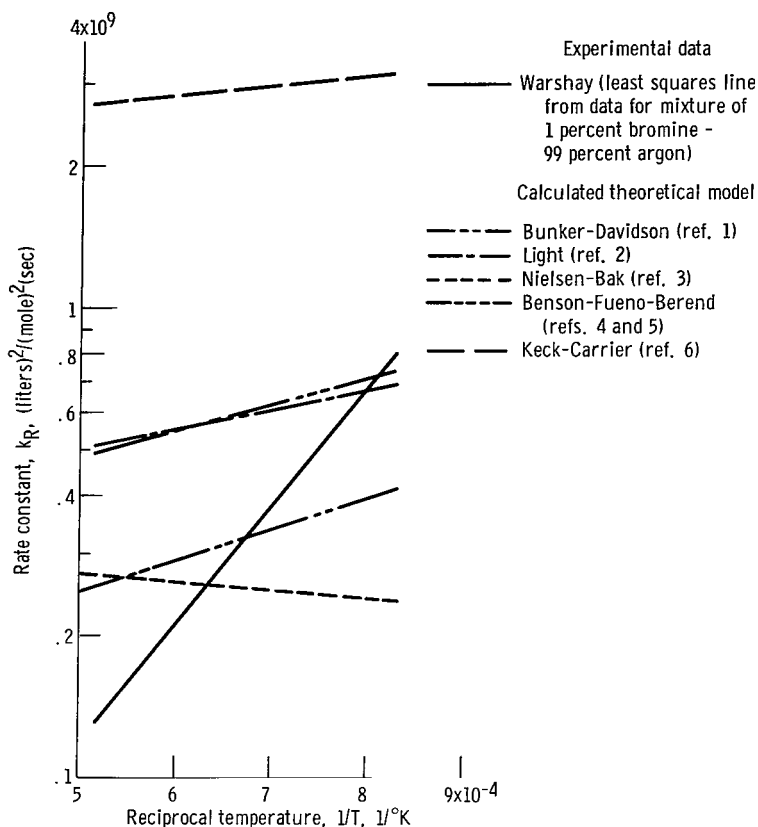


Figure 9. - Rate constants for recombination of bromine in bromine - argon mixture.

bromine dissociation in the presence of argon was 31.5 kilocalories as compared with 45.5 kilocalories for the dissociation energy. The data of this experiment are not the only bases for this conclusion. Although there is disagreement among the results of past investigators of bromine dissociation, in each case the slope of the experimental line is not as steep as it would be for  $E_a = D_0$ . Furthermore, the results of other dissociation experiments (refs. 10, 14, 17, 19, 26, and 27) of polyatomic, as well as diatomic, molecules indicate that  $E_a < D_0$  when the data are expressed in the simple collisional form.

## Collision Partner Effects Upon Relative Dissociation Rates

The results of the present investigation permit an evaluation of the predictions for each model of the effects of the noble-gas collision partner upon bromine dissociation rates. These are the rates of dissociation of bromine in the presence of neon, argon, and krypton. The use of relative rates focuses attention upon the collision partner effects. Table II can be used for a comparison of these relative dissociation rates. With this table three observations can be made for each model. First, the degree to which each

TABLE II. - COMPARISON OF EXPERIMENTAL AND CALCULATED BROMINE RELATIVE DISSOCIATION RATE CONSTANTS FOR ARGON, NEON, AND KRYPTON COLLISION PARTNERS

Source of rate constants	Temperature, T, °K	Ratio of dissociation rate constants		Qualitative evaluation of model		
		$k_{D, Ne}/k_{D, Ar}$	$k_{D, Kr}/k_{D, Ar}$	Closeness to experimental results	Mass effect	Temperature effect
1. Warshay <sup>a</sup>	300	----	----	----	----	----
	1200	0.87	0.84			
	1800	.88	1.14			
2. Nielsen-Bak <sup>b</sup>	300	0.81	1.03	Good	Moderate	None
	1200	.81	1.03			
	1800	.81	1.03			
3. Light <sup>b</sup>	300	0.75	0.93	Poor	Inverse effect on krypton	Opposite effects on neon and krypton
	1200	1.07	.84			
	1800	1.12	.82			
4. Bunker-Davidson <sup>b</sup>	300	0.26	1.45	Poor	Strong	None
	1200	.27	1.48			
	1800	.27	1.48			
5. Keck-Carrier <sup>b</sup>	300	----	----	Fair	None	None
	1200	1	1			
	1800	1	1			
6A. Benson-Fueno-Berend <sup>b</sup>	300	----	----	Best	Moderate	None
	1200	0.86	1.13			
	1800	.86	1.13			
6B. Benson-Fueno-Berend <sup>b</sup>	300	----	----	Good	Moderate	Moderate
	1200	0.72	1.08			
	1800	.87	1.21			

<sup>a</sup>Experimental data.

<sup>b</sup>Calculated theoretical model.

model predicts experimental relative bromine dissociation results is shown. Second, the degree of influence of the mass of the noble-gas collision partner is considered. Third, the influence of temperature upon the relative rates is noted. All three of these observations are summarized in table II.

Four the the models, 2, 4, 5, and 6A, display no significant temperature effect upon the relative rates. In fact, the Keck-Carrier model 5 predicts no effect whatsoever of collision partner upon relative reaction rates. In table II, the values for this model are inferred from theoretical calculations in reference 6 in which for each of six diatomic

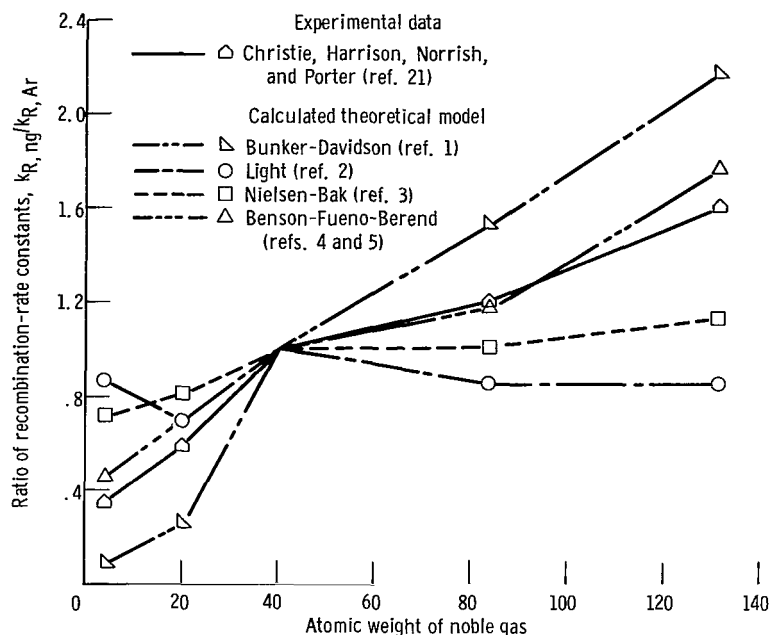


Figure 10. - Experimental and theoretical values for ratio of recombination-rate constant for iodine in presence of noble gas third body to that in presence of argon.

molecules the nature of the noble gas had no effect upon the rate. This finding is surprising because the Keck-Carrier theoretical rate constant expression does include parameters which are dependent upon the collision partner. At the other extreme is the Bunker-Davidson model 4, which, in comparison with the observed results, exaggerates the influence of collision partner upon reaction rates.

The Benson-Fueno-Berend model makes the predictions which are closest to observed results. Two cases are listed for this model. In case 6A the authors' calculated results are taken at face value; the values were read directly from a figure in which it is assumed that the efficiencies of the collision partners do not change with temperature. However, in the same article the authors indicate that there is a small effect of temperature. From figures 12, 15, and 16 in reference 5, it was possible to calculate a somewhat different set of collision partner efficiencies which is labeled 6B in table II. These values which display a small temperature dependency match the observed values reasonably well, although not as well as those of 6A.

## Collision Partner Effects Upon Relative Recombination Rates

From figure 10 a comparison can be made of the ability of each model to predict the influences of the inert noble gases on iodine recombination rates. The experimental results of Christie, Harrison, Norrish, and Porter (ref. 21) are used as the standard of comparison because they are considered the most accurate available. In addition, their

investigation covered the largest number of noble gases. The abscissa merely identifies the noble-gas third body; the gases are arranged in order of atomic weight. For simplicity, the data are joined by straight line segments. In every case the model of Benson, Fueno, and Berend predicts values closest to experimental values. The other recombination model (Bunker-Davidson) makes predictions which have the proper trend but which exaggerate the effect of mass. Of the two dissociation models, the predictions of Nielsen and Bak are closer to experimental values than are the predictions of Light.

The theoretical rate data presented in figures 8 to 10 and in table II were either obtained from the original model references themselves or else calculated from the equations presented in these references. Several of the final theoretical equations are expressed in terms of molecular properties such as collision cross sections and attractive energies. Therefore, the particular set of properties used may have a considerable effect upon the calculated rates, especially the relative rates. This was particularly true of the Nielsen-Bak model, which was strongly dependent upon the values of the cross sections. The major source of molecular properties was reference 28; reference 29 was used to a lesser extent.

## CONCLUDING REMARKS

The improvement in the reliability of these results is attributed to the efforts made to uncover and diminish weaknesses of past investigations. Major efforts were devoted to the avoidance of bromine-metal contact, to the maintenance of a stable incident light intensity  $I_0$ , and to the reduction of the enthalpy effect to a minor influence. Of the remaining sources of error, two that are difficult to eliminate completely are associated with the non-ideal shock-wave behavior and the measurement of initial slopes from oscilloscope traces.

The model best able to predict the effects of noble gas collision partners upon halogen recombination and dissociation is the Benson-Fueno-Berend mechanism of atom recombination by consecutive vibrational deactivation. However, this conclusion may have to be altered as different halogen - noble-gas systems are investigated experimentally, as totally new models are proposed, and as existing models are modified. For instance, it has been reported that both the Benson-Fueno-Berend and the Keck-Carrier models are presently undergoing revisions. Also, it will be well for those who are developing theoretical kinetic models to consider that for many substances undergoing dissociation at high temperatures it is inappropriate to assume a simple collisional model in which the activation energy  $E_a$  is equal to the dissociation energy  $D_0$ .

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, April 5, 1966.

## REFERENCES

1. Bunker, Don L.; and Davidson, Norman: On the Interpretation of Halogen Atom Recombination Rates. *J. Am. Chem. Soc.*, vol. 80, no. 19, Oct. 7, 1958, pp. 5090-5096.
2. Light, John C.: Dissociation of Gaseous Diatomic Molecules: Classical Adiabatic Scattering Approach. *J. Chem. Phys.*, vol. 36, no. 4, Feb. 1962, pp. 1016-1030.
3. Nielsen, Svend Erik; and Bak, Thor A.: Hard-Sphere Model for Dissociation of Diatomic Molecules. *J. Chem. Phys.*, vol. 41, no. 3, Aug. 1964, pp. 665-674.
4. Benson, Sidney W.; and Fueno, Takayuki: Mechanism of Atom Recombination by Consecutive Vibrational Deactivations. *J. Chem. Phys.*, vol. 36, no. 6, Mar. 1962, pp. 1597-1607.
5. Benson, Sidney W.; and Berend, George C.: Vibrational Energy Exchange of Highly Excited Anharmonic Oscillators. *J. Chem. Phys.*, vol. 40, no. 5, Mar. 1964, pp. 1289-1298.
6. Keck, James; and Carrier, George: Diffusion Theory of Nonequilibrium Dissociation and Recombination. *J. Chem. Phys.*, vol. 43, no. 7, Oct. 1965, pp. 2284-2298.
7. Nikitin, E. E.; and Sokolov, N. D.: Theory of Thermal Second-Order Decomposition of Molecules. *J. Chem. Phys.*, vol. 31, no. 5, Nov. 1959, pp. 1371-1375.
8. Keck, James C.: Variational Theory of Dissociation and Recombination. Rept. No. 58, Avco Corp., June 1959.
9. Palmer, Howard B.: Chemical Kinetics and Hypersonic Flow. Rept. No. PSU-11-P, Penn. State Univ., Aug. 1964.
10. Britton, Doyle; and Davidson, Norman: Shock Waves in Chemical Kinetics. Rate of Dissociation of Molecular Bromine. *J. Chem. Phys.*, vol. 25, no. 5, Nov. 1956, pp. 810-813.
11. Palmer, H. B.; and Hornig, D. F.: Rate of Dissociation of Bromine in Shock Waves. *J. Chem. Phys.*, vol. 26, no. 1, Jan. 1957, pp. 98-105.
12. Britton, Doyle: Shock Waves in Chemical Kinetics: Further Studies in the Rate of Dissociation of Bromine. *J. Chem. Phys.*, vol. 34, no. 6, June 1960, pp. 742-748.
13. Johnson, Charles D.; and Britton, Doyle: Shock Waves in Chemical Kinetics: The Use of Reflected Shock Waves. *J. Chem. Phys.*, vol. 38, no. 7, Apr. 1963, pp. 1455-1462.



14. Britton, Doyle; Davidson, Norman; Gehman, William; and Schott, Garry: Shock Waves in Chemical Kinetics: Further Studies on the Rate of Dissociation of Molecular Iodine. *J. Chem. Phys.*, vol. 25, no. 5, Nov. 1956, pp. 804-809.
15. Glass, I. I.; Martin, W.; and Patterson, G. N.: A Theoretical and Experimental Study of the Shock Tube. Rept. No. 2, Univ. of Toronto, Nov. 1953.
16. Wray, Kurt L.: Shock-Tube Study of the Coupling of the O<sub>2</sub>-Ar Rates of Dissociation and Vibrational Relaxation. *J. Chem. Phys.*, vol. 37, no. 6, Sept. 1962, pp. 1254-1263.
17. Jacobs, T. A.; and Geidt, R. R.: Dissociation of Cl<sub>2</sub> in Shock Waves. *J. Chem. Phys.*, vol. 39, no. 3, Aug. 1963, pp. 749-756.
18. Sulzer, P.; and Wieland, K.: Intensitätsverteilung eines kontinuierlichen Absorptions-spektrums in Abhängigkeit von Temperatur und Wellenzahl. (Intensity Distribution of a Continuous Adsorption Spectrum and Its Dependence on Temperature and Wave Number.) *Helv. Phys. Acta*, vol. 25, 1952, pp. 653-676.
19. Hiraoka, Hiroyuki; and Hardwick, R.: Dissociation of Halogens in Shock Waves. *J. Chem. Phys.*, vol. 36, no. 7, Apr. 1962, pp. 1715-1720.
20. Diesen, R. W.: Mass Spectral Studies of Kinetics Behind Shock Waves. III. Thermal Dissociation of Fluorine. Tech. Rept. No. SL151879, The Dow Chemical Co., June 22, 1965.
21. Christie, Margaret I.; Harrison, Anna J.; Norrish, R. G. W.; and Porter, G.: The Recombination of Atoms. II. Causes or Variation in the Observed Rate Constant for Iodine Atoms. *Proc. Roy. Soc., ser. A*, vol. 231, no. 1187, Sept. 20, 1955, pp. 446-457.
22. Russell, K. E.; and Simons, J.: Studies in Energy Transfer. I. The Combination of Iodine Atoms. *Proc. Roy. Soc., ser. A*, vol. 217, no. 1129, Apr. 8, 1953, pp. 271-279.
23. Rink, John P.; Knight, Herbert T.; and Duff, Russell E.: Shock Tube Determination of Dissociation Rates of Oxygen. *J. Chem. Phys.*, vol. 34, no. 6, June 1961, pp. 1942-1947.
24. Rink, John P.: Relative Efficiencies of Inert Third Bodies in Dissociating Oxygen. *J. Chem. Phys.*, vol. 37, no. 2, Jan. 1962, pp. 572-573.
25. Rink, John P.: Shock Tube Determination of Dissociation Rates of Hydrogen. *J. Chem. Phys.*, vol. 36, no. 1, Jan. 1962, pp. 262-265.

26. Britton, Doyle; Davidson, Norman; and Schott, Garry: Shock Waves in Chemical Kinetics: The Rate of Dissociation of Molecular Iodine. Discussions Faraday Soc., vol. 17, 1954, pp. 58-68.
27. Brabbs, Theodore A.; Belles, Frank E.; and Zlatarich, Steven A.: Shock-Tube Study of Carbon Dioxide Dissociation Rate. J. Chem. Phys., vol. 38, no. 8, Apr. 1963, pp. 1939-1944.
28. Svehla, Roger A.: Estimated Viscosities and Thermal Conductivities of Gases at High Temperatures. NASA TR R-132, 1962.
29. Hirschfelder, Joseph O.; Curtiss, Charles F.; and Bird, R. Bryon: Molecular Theory of Gases and Liquids. John Wiley & Sons, Inc., 1954.

*"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."*

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

## NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

**TECHNICAL REPORTS:** Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

**TECHNICAL NOTES:** Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

**TECHNICAL MEMORANDUMS:** Information receiving limited distribution because of preliminary data, security classification, or other reasons.

**CONTRACTOR REPORTS:** Technical information generated in connection with a NASA contract or grant and released under NASA auspices.

**TECHNICAL TRANSLATIONS:** Information published in a foreign language considered to merit NASA distribution in English.

**TECHNICAL REPRINTS:** Information derived from NASA activities and initially published in the form of journal articles.

**SPECIAL PUBLICATIONS:** Information derived from or of value to NASA activities but not necessarily reporting the results of individual NASA-programmed scientific efforts. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

*Details on the availability of these publications may be obtained from:*

SCIENTIFIC AND TECHNICAL INFORMATION DIVISION  
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
Washington, D.C. 20546